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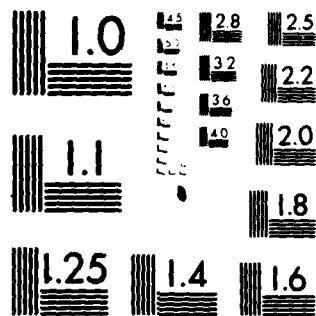
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RESEARCH ON NEW SOLID SUPERIONIC CONDUCTORS CONTAINING CU⁺, BA⁺⁺—ETC(U)
FEB 82 D F SHRIVER, D H WHITMORE AFOSR-77-3227

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Final Annual Report for 1981

Research on New Solid Superionic Conductors

Containing Cu^+ , Ga^+ , In^+ , and Tl^+

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co-principal investigators

Northwestern University
February 1982

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MATTHEW J. KERPER
Chief, Technical Information Division

We summarize here some of the general accomplishments in this research project along with the specific progress in this last year. The overall objectives of this study included: (1) the synthesis of new solid electrolyte materials which differ in composition and mobile ion from those currently available, with special emphasis on complex salts containing mobile Cu(I), Ga(I), In(I), and Th(I) ions, (2) the screening of new solid materials for high ionic conductivity coupled with low electronic conductivity; and (3) detailed characterization studies of the new solid electrolyte materials which were aimed at developing an understanding of charged particle transport, and the effects of temperature and impurities on transport properties.

In order to develop a deeper understanding of the role of electronic structure of the cation on fast ion transport in solids, we investigated a series of solid electrolytes of the formula A_2MX_4 ($A^+ = Cu^+, Ag^+, In^+$, or Tl^+ ; $M^{2+} = Zn^{2+}, Cd^{2+}$, or Hg^{2+} ; $X = Br^-$ or I^-). Electrical measurements on these materials show consistently lower conductivity for the $d^{10}s^2$ ions, In^+ and Tl^+ , than for the d^{10} ions, Cu^+ and Ag^+ . A single crystal x-ray investigation of the structure for Tl_2ZnI_4 demonstrates that the cation resides in a low symmetry 5-coordinate environment. Raman spectroscopy and x-ray powder diffraction suggest a similar structure for the corresponding In^+ salt. By contrast, structural data in the literature indicate that Cu^+ and Ag^+ reside in tetrahedral sites in their respective compounds. These comparisons suggest that the lower conductivity of the $d^{10}s^2$ ions arise from the structural differences. The structural differences are imposed by the unsymmetrical polarization of the $d^{10}s^2$ ions which contrasts with the symmetrical polarization of d^{10} ions.



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This earlier work prompted spectroscopic investigations and electronic structure calculations on the influence exerted by the cation on the energy of the transition state for ion transport. To address this issue, ab initio Hartree-Fock LCAO-MO calculations were performed on MI_4 arrays. The ground state structure was taken as the cation residing in the center of a tetrahedral I_4 array and the transition state was modeled by the ion in the face of the I_4 array. Lower energies were found for the movement of the d^{10} ions into the face of the iodide tetrahedron. In a classical sense this result arises from the energetically favorable quadrupolar polarization of the d^{10} ions which lowers the energy of the local D_{3h} symmetry MI_4 array for the cation in the tetrahedral face. The $d^{10}s^2$ ions on the other hand are most susceptible to dipolar polarization, which is not compatible with D_{3h} local symmetry.

These results demonstrate that the detailed electronic structure of the cation can have a profound influence on ion transport. Furthermore, our results indicate that the low mobility of the group III monovalent ions results from the fundamental general causes and therefore these ions are not attractive for further exploration as mobile species in solid electrolytes.

By contrast, the Ag^+ and Cu^+ conductors appear to be quite promising. The best solid copper ion conductors known to date are the compounds $Cu_{16}Rb_4Cl_{13}I_7$ and $Cu_{16}Rb_4Cl_{12}I_8$; these possess ionic conductivities at $25^\circ C$ of $0.34 (\Omega \text{ cm})^{-1}$ and $0.44 (\Omega \text{ cm})^{-1}$ and activation energies of 0.07 and 0.15 eV, respectively. However, for these materials to be useful as solid electrolytes in commercial primary cells, they must also exhibit negligible small specific electronic conductivities. Measurements of the electronic conductivities of these copper ion salts were made with the aid of a d.c.

polarization technique. The concentrations of electron holes in these materials were determined as a function of temperature from an analysis of transient currents in such polarization cells. The specific conductivity for the electron holes exhibited an activation energy of 1 eV and a room-temperature value of $5 \times 10^{-16} (\Omega \text{ cm})^{-1}$. The hole concentrations ranged from 10^9 cm^{-3} at 25°C to 10^{11} cm^{-3} at 130°C, and the transport number for the electron holes ranged from 10^{-15} at 25°C to 10^{-11} at 140°C. Since the partial electron hole conductivities and transport numbers are negligibly small at all temperatures where these phases are solids and their Cu^+ ion conductivities are outstanding, these compounds should be excellent solid electrolytes in commercial primary cell applications.

A new research effort in polymer electrolytes was launched under AFOSR support. The specific systems studied have the approximate composition MX-4PEO (M is an alkali metal ion, X is a large anion, and PEO is the repeat unit of polyethylene oxide). These are promising materials for application in solid state electrochemical devices. In contrast to inorganic electrolytes, the highly compliant polymer electrolyte should maintain good contact with the electrode materials.

In order to understand the structures and dynamics of these materials we performed detailed infrared and Raman spectroscopic investigations. Mid-infrared spectra provided information on the conformation of the polymer backbone, and high frequency Raman data indicated the polymer is wrapped around the cations. Far-infrared spectra reveal the presence of cation translational modes for which the frequencies scale approximately as the square root of the mass of the cation, and which have negligible dependence

on the nature of the anion. These results along with the published x-ray fiber repeat distances, and steric considerations, are best fit by a model in which the cations reside inside helical spirals of the polymer. The anions are thought to reside outside of these helices.

PUBLICATIONS (cumulative):

1. "Trends in Heavy-Metal Solid State Ionic Conductors: A Comparison of Cu^+ , Ag^+ , In^+ , and Tl^+ Transport," R. L. Ammlung, R. P. Scaringe, J. A. Ibers, D. F. Shriver, and D. H. Whitmore, J. Solid State Chem. **29**, 401 (1979).
2. "Indium(I) and Thallium(I) Transport in Halide Lattices," D. F. Shriver, M. A. Ratner, R. Ammlung, J. I. McOmber, and D. H. Whitmore, Proc. Int. Conf. on Fast Ion Transport in Solids, ed. by P. Vashishta, J. N. Mundy and G. K. Shenoy (Amsterdam: North-Holland, 1979) p. 515.
3. "Ab-Initio Electronic Structure Studies of Mobility Paths in Fast Ion Conductors. I." J. I. McOmber, S. Topiol, M. A. Ratner, D. F. Shriver, and J. Moskowitz, J. Phys. Chem. Solids, **41**, 447 (1980).

"Polarization Study on the Solid Electrolyte $\text{Cu}_{16}\text{Rb}_4\text{I}_{7+x}\text{Cl}_{20-(7+x)}$ ($0 < x < 1$)," C. Chaney, D. F. Shriver and D. H. Whitmore, Solid State Ionics **5**, 505 (1981).
4. "Vibrational Spectroscopy and Structure of Polymer Electrolytes, Poly(ethylene Oxide) Complexes of Alkali Metal Salts", B. L. Papke, M. A. Ratner, and D. F. Shriver, J. Phys. Chem. Solids, **42** 493 (1981).
5. Ph.D. Thesis: R. L. Ammlung, "Synthesis and Properties of Fast Ion Conductors of the Heavy Metal Halide Compounds of Monopositive Metal Ions", Northwestern University, 1979.
6. Ph.D. Thesis: J. I. McOmber, "Vibrational Spectroscopic and Theoretical Investigations of Heavy Metal Halide Fast Ion Conductors", Northwestern University, 1981. (The expenses for theoretical calculations associated with this research were largely supported from AFOSR funds).
7. Ph.D. Thesis: B. L. Papke, "Vibrational Spectroscopy, Structure, and Ion Transport in Complexes of Poly(ethylene oxide) with Alkali Metal Salts: A Class of Polymeric Solid Electrolytes", Northwestern University, 1982. (Thesis defended in 1981).

8. Ph.D. Thesis: C. Chaney, "Ionic and Electronic Conduction Processes in the Solid Electrolyte $\text{Cu}_{16}\text{Rb}_4\text{I}_{7+x}\text{Cl}_{20-(7+x)}$ ($0 < x < 1$)," Northwestern University, 1982.

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